Photoinduced transformations of indole and 3-formylindole monomers isolated in low-temperature noble-gas matrices

Igor Reva,1 Leszek Lapinski,2 A. J. Lopes Jesus,1,3 and Maciej J. Nowak2,a)1
1CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
2Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
3CQC, Faculty of Pharmacy, University of Coimbra, 3004-295 Coimbra, Portugal

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Photochemical transformations were studied for monomers of indole and 3-formylindole isolated in low-temperature noble-gas matrices. Upon UV (λ > 270 nm) irradiation of indole trapped in argon and neon matrices, the initial 1H-form of the compound converted into the 3H-tautomer. Alongside this photoinduced hydrogen-atom transfer, an indolyl radical was also generated by photodetachment of the hydrogen atom from the N1—H bond. Excitation of 3-formylindole isolated in an argon matrix with UV (λ > 335 nm) light led to interconversion between the two conformers of the 1H-tautomer, differing from each other in the orientation of the formyl group (cis or trans). Parallel to this conformational phototransformation, the 3H-form of the compound was generated in the 1H → 3H phototautomeric conversion. The photoproducts emerging upon UV irradiation of indole and 3-formylindole were identified by comparison of their infrared spectra with the spectra calculated for candidate structures. Published by AIP Publishing. https://doi.org/10.1063/1.5003326

I. INTRODUCTION

Various molecules exhibiting important biological activities are constituted by an indole core and a substituent at the 3-position.1–3 Two well-known examples of such molecules are the aminoacid tryptophan and the neurotransmitter serotonin. Enzymatic deamination of tryptophan yields several 3-substituted indole analogues, such as indole-3-acetaldehyde and indole-3-acetic acid (IAA).4 IAA is an important hormone and an integral regulator of cell division, expansion, and differentiation in plants.5,6 and in phytoplankton.7 Moreover, indoles are important scaffolds in a large diversity of synthetic drugs, which are clinically used for anti-inflammatory, analgesic, anticancer, and antidepressant therapeutic applications.8 The relevance of these molecules in regard to the role they play as chromophores in bio-macromolecules (e.g., tryptophan in proteins)9 renders the study of the light-induced processes in these systems an important matter from both theoretical and practical viewpoints. The photochemical and photophysical processes triggered by UV-excitation of indoles have attracted great interest.10–13

It has long been recognized that photophysical processes in UV-excited indoles are governed by two low-energy 1π* singlet excited states, which are commonly designated as 1Lα and 1Lβ.14–16 More recently, it has been theoretically predicted that the lowest 1π* excited state of dissociative character plays an important role in the hydrogen-atom photodetachment from the N1—H bond.17–19 This prediction was confirmed by photofragment translational spectroscopy and pump-probe experiments, where slow and fast hydrogen atoms were observed to dissociate from UV-excited molecules of indole seeded in supersonic jet expansions.20–24 The partner fragment to the hydrogen atom photodetached from indole is the indolyl radical.20 The indolyl radical is a topic in its own right. It mimics the tryptophan radical which is currently believed to participate in electron transfer in proteins25 and conduct to DNA-peptide cross-linking.26 In condensed media, either under biological or under laboratory conditions, the radicals may recombine with H atoms, yielding back the starting material or resulting in new prototropic tautomers. Indole may adopt nine prototropic tautomers. The tautomer with the labile hydrogen atom connected to the N1 nitrogen atom is called 1H-indole, Fig. 1(a). In the other tautomers, designated as 2H-indole, . . . , 9H-indole, this hydrogen atom migrates to atoms C2, . . . , C9. The form 3H-indole (also called indolenine) was the subject of several investigations.27–31 Indolenine was generated by pyrolysis of gaseous indole29 or, alternatively, by photodecomposition of N-indoliny lacetophenone in aqueous solution.30 At temperatures above −50 °C, indolenine rapidly transforms back into 1H-indole. Therefore, 3H-indole was very difficult to be spectroscopically characterized using conventional sampling techniques. For indole in neat crystalline, liquid, or gas phase, only the 1H-tautomer was observed so far by infrared, Raman, or microwave spectroscopy.32–34

Despite the biological relevance of indoles, unimolecular photochemical transformations of these molecules have not been thoroughly investigated. The current work is focused on the photoinduced structural transformations of indole and 3-formylindole (3FOI, a representative of 3-substituted indoles) isolated in cryogenic noble-gas matrices (Ar and Ne). The main objective of this study is the investigation of the photochemical transformations induced by UV-excitation of isolated monomers of indole. The photoprocesses observed for the parent molecule of indole were compared with those found

Author to whom correspondence should be addressed: mjnow@ifpan.edu.pl
for the 3-substituted indole derivative 3FOI. An additional aim of the present work is the investigation of photoinduced internal rotation of the formyl group in 3FOI to the C3 atom of the indole ring. Figs. 1(b) and 1(c). The study on this latter topic is complementary to the previous studies on the UV-induced rotamerization of a formyl group connected to pyrrole\textsuperscript{35} or benzene\textsuperscript{36} rings.

II. COMPUTATIONAL DETAILS

The geometries of all prototropic and conformational isomers of indole and 3-formylindole (3FOI) were fully optimized using the density functional theory (DFT) with Becke’s three-parameter exchange functional, combined with the Lee, Yang, and Parr correlation functional (B3LYP)\textsuperscript{37–39} and with the standard 6-311++G(d,p) basis set. Further energy calculations were carried out for all structures by using more sophisticated theoretical methods combined with the same basis set. For the prototropic tautomers of indole, the relative energies were calculated by using the quadratic configuration interaction with single and double excitations (QCISD) method\textsuperscript{40} at geometries optimized at the same (QCISD) level, while for all 3FOI isomers, the relative energies were computed with the QCISD method at geometries optimized at the DFT(B3LYP) level.

DFT(B3LYP)/6-311++G(d,p) harmonic vibrational frequencies and IR intensities were calculated for all structures on the geometries optimized at the same level. The computed harmonic vibrational wavenumbers were scaled down by a factor of 0.98 (for wavenumbers lower than 3200 cm\textsuperscript{-1}) or by a factor of 0.95 (for wavenumbers higher than 3200 cm\textsuperscript{-1}). For 1H-indole and for the two conformers of the 1H-tautomer of 3FOI (1H-cis and 1H-trans), anharmonic vibrational calculations were also carried out at the same level. The normal modes, calculated for 1H-indole, were analyzed in terms of the Potential Energy Distribution (PED). For this purpose, a set of internal coordinates (listed in Table S1 of the supplementary material) has been defined. The calculated force constants with respect to Cartesian coordinates were transformed into the force constants with respect to internal coordinates and the potential energy distribution (PED) matrix was calculated.\textsuperscript{41}

The barriers for rotation of the formyl group in 1H and 3H tautomers of 3FOI were assessed by performing, at the MP2\textsuperscript{42} and DFT(B3LYP) levels, relaxed potential energy scans. In these computations, the O11=C10—C3=C2 dihedral angle was chosen as the driving coordinate. All quantum-chemical computations were carried out with the Gaussian 09 (revision D.01) program package,\textsuperscript{43} and for visualization of results, the ChemCraft software was used.\textsuperscript{44} Natural Bond Orbital (NBO) calculations,\textsuperscript{45} including a Natural Resonance Theory (NRT) analysis, were also performed for some selected structures at the DFT(B3LYP)/6-311++G(d,p) level by using the NBO 5.0 program\textsuperscript{46} implemented in GAMESS.\textsuperscript{47}

III. EXPERIMENTAL PROCEDURES

The samples of indole (99%) and 3-formylindole (3FOI, 98%), used in the current study, were supplied by TCI Europe and Sigma-Aldrich, respectively. Before matrix-isolation experiment, the solid sample of indole was placed in a glass tube connected through a needle valve to the vacuum chamber of a cryostat with a Sumitomo SRDK-408D2 closed-cycle cooler. With the cryostat still at room temperature, the glass tube was degassed to remove remaining air and volatile impurities. To prepare a low-temperature matrix containing indole monomers, vapor of the compound (over a solid sample kept at ∼285 K in a glass tube equipped with a regulating valve) was co-deposited with a large excess of argon or neon (Linde AG, purity 6.0) onto a CsI optical substrate cooled to 15 K (for Ar) or 5 K (for Ne). Matrices containing monomers of 3FOI were prepared in a similar way. The volatility of 3FOI is lower than that of indole. Therefore, to obtain sufficient flux of the 3FOI vapor coming to the cold CsI window, the solid compound was electrically heated (to 350 K) in a miniature glass oven placed inside the vacuum chamber of the cryostat.

Infrared spectra of the matrix-isolated compounds were recorded with a Thermo Nicolet iS50R FTIR spectrometer equipped with a KBr beam splitter and a DTGS/KBr detector, for measurements in the 4000-500 cm\textsuperscript{-1} region; with a CaF\textsubscript{2} beam splitter and an InGaAs detector, for measurements in the 8000–4000 cm\textsuperscript{-1} region; or with a "solid substrate" beam splitter and a DTGS/PE detector, for measurements in the 600-200 cm\textsuperscript{-1} region. The FTIR spectra were collected with a resolution of 0.5 cm\textsuperscript{-1} (4000-200 cm\textsuperscript{-1} range) or 1 cm\textsuperscript{-1} (8000-4000 cm\textsuperscript{-1} range). Matrix-isolated monomers of indole or 3FOI were irradiated with UV light emitted from a high-pressure HBO200 mercury lamp fitted with a water filter and with a long-pass WG345, WG335, WG320, WG295, or UG11 Schott filter, transmitting light with λ > 345, 335, 320, 295, or 270 nm, respectively. The transmission spectra of these filters are presented in Fig. S1 of the supplementary material.

Matrix-isolated monomers of 3FOI were also irradiated with monochromatic near-infrared (NIR) light provided by a frequency-tunable Toptica DL100pro continuous wave diode laser (FWHM < 1 MHz, output power ∼40 mW). The wavelengths of the NIR light were measured with a HighFiniess WS-5 wavelength meter. Irradiation time at a particular NIR wavelength was 30 min.

IV. RESULTS AND DISCUSSION

A. The most stable isomer of indole and its infrared spectrum

Relative energies of prototropic tautomers of indole (see structures in Table S2 in the supplementary material) have been
calculated with the QCISD/6-311++G(d,p) method at geometries optimized at the same QCISD/6-311++G(d,p) level. The obtained results (given in Table S3 of the supplementary material) are graphically presented in Fig. 2. The computed relative energies show that the most stable tautomeric form of the compound is 1H-indole (Fig. 1), with the labile hydrogen atom attached to N1. The high relative stability of this tautomer can be explained by a pronounced π-electron delocalization (aromaticity) within the indole ring of the 1H-structure and by a reduced π-electron delocalization in other forms, where the labile hydrogen atom is attached to one of the ring carbon atoms. The energy of 3H-indole is predicted to be higher by 25 kJ mol$^{-1}$ than that of 1H-indole. Relative energy as high as that excludes any non-negligible population of this tautomer in the gas phase and consequently in the deposited cryogenic matrix. On the other hand, the energy of 3H-indole is significantly lower than that of the remaining prototropic tautomers, which have energies higher by more than 100 kJ mol$^{-1}$ with respect to the 1H-form (Fig. 2). In that sense, 3H-indole, having a moderately high relative energy, is exceptional among the tautomers with the labile hydrogen atom moved from N1 to any of the carbon atoms. This can be attributed to the fact that in 3H-indole, the full aromaticity within the benzene ring is preserved, whereas in 2H, 4H, . . . , 9H structures, aromaticity of the benzene ring is disrupted (see Table S2 of the supplementary material).

The infrared spectra of indole monomers isolated in low-temperature Ar and Ne matrices are presented in Fig. 3. The experimental spectra are well reproduced by the theoretical spectrum calculated, at the DFT(B3LYP)/6-311++G(d,p) level, for 1H-indole. This allowed a reliable assignment of the experimental IR bands to the theoretically calculated normal modes (Table I). In the high-wavenumber region of the spectrum, the band due to stretching vibration of the N1-H group ($\nu$N1H) was observed at 3522 cm$^{-1}$ (Ne) and at 3523 cm$^{-1}$ (Ar). These values match well the vNH frequency of 3525 cm$^{-1}$, observed for indole in the gas phase. In the low-wavenumber region, a characteristic band due to out-of-plane, wagging vibration of N1-H ($\gamma$N1H) was found at 390 cm$^{-1}$ (Ne) and at 395 cm$^{-1}$ (Ar). The infrared band, appearing in the experimental spectra at 796 cm$^{-1}$ (Ne) and 804 cm$^{-1}$ (Ar), has no counterpart in the theoretical spectrum calculated within the harmonic approximation. However, in this wavenumber range, a vibration due to 2$\gamma$N1H overtone, with infrared intensity as high as 46 km mol$^{-1}$, is predicted by anharmonic vibrational calculations, carried out at the DFT(B3LYP)/6-311++G(d,p) level (see Table I). Intensities of 2$\gamma$N1H transitions are exceptionally high as for overtones.

FIG. 2. Relative energies of the prototropic tautomers of indole (black bars), as well as 3FOI isomers: 3FOI-trans (blue bars) and 3FOI-cis (red bars). The energies were calculated with the QCISD/6-311++G(d,p) method, at geometries optimized at the same QCISD/6-311++G(d,p) level (for indole) and at the DFT(B3LYP)/6-311++G(d,p) level (for 3FOI). The relative energies were calculated with respect to the energy of the most stable 1H-tautomer (for 3FOI, it is the 3FOI-trans form). For the 3H-tautomer of 3FOI, the red and the blue bars represent the energies of the ac$^-$ and ac$^+$ conformers, respectively (see the structures presented in Table S2 and the calculated energies in Table S3 in the supplementary material).

FIG. 3. (a) Experimental IR spectrum of indole monomers isolated in a neon matrix at 5.5 K; (b) experimental IR spectrum of indole monomers isolated in an argon matrix at 15 K; (c) theoretical IR spectrum of 1H-indole calculated within the harmonic approximation at the DFT(B3LYP)/6-311++G(d,p) level. The theoretical wavenumbers higher than 3200 cm$^{-1}$ were scaled by 0.95, and the wavenumbers lower than 3200 cm$^{-1}$ were scaled by 0.98. In the experimental spectra, the absorptions at 796 cm$^{-1}$ (Ne) and 804 cm$^{-1}$ (Ar) (marked with asterisks) correspond to the 2$\gamma$NH overtone of the out-of-plane wagging vibration of the NH group; the bands due to the fundamental $\gamma$NH vibration appear in the experimental spectra at 390 cm$^{-1}$ (Ne) and 395 cm$^{-1}$ (Ar), see Table I. Truncated bands in all frames are marked with tildes (\~{}).
TABLE I. Experimental positions (\textdegree cm\(^{-1}\)) and relative integrated intensities (I) of the absorption bands in the infrared spectrum of indole isolated in argon and neon matrices, compared with the wavenumbers (\textdegree cm\(^{-1}\)), absolute intensities (Ath/km mol\(^{-1}\)), and potential energy distribution (PED, %) calculated for the 1H-tautomer of indole at the DFT(B3LYP)/6-311+G(d,p) level of theory.

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^aExperimental intensities (initially measured in arbitrary units of absorbance) were normalized by dividing all of them by a factor obtained as a ratio \(\Sigma_{exp}/\Sigma_{calc}\), where \(\Sigma_{exp}\) is the sum of integrated intensities of such experimental absorption bands that were unequivocally assigned to the theoretical modes and \(\Sigma_{calc}\) is the sum of absolute infrared intensities calculated for the bands due to the corresponding theoretical modes.

^bTheoretical positions of the absorption bands were scaled by 0.95 (above 3200 cm\(^{-1}\)) and 0.98 (below 3200 cm\(^{-1}\)).

^cPEDs lower than 10% are not included. Definition of internal coordinates is given in Table S1 (in the supplementary material). See Fig. 1 for atom numbering.

^dAssignments supported by the results of the anharmonic vibrational calculations (see Table S4 and Fig. S2 in the supplementary material).

^eGas phase data. See Ref. 48.
Therefore, infrared bands due to \(2\gamma\)CH overtones were also observed in the spectra of other compounds structurally similar to indole (e.g., 7-azaindole\(^{59}\)).

Infrared absorptions due to overtone and combinational transitions were also observed in the 2100-1540 cm\(^{-1}\) range of experimental spectra of indole isolated in Ne and Ar matrices (Fig. S2 of the supplementary material). Most of these bands are fairly well reproduced by the anharmonic DFT(B3LYP)/6-311++G(d,p) calculation. Their assignment is provided in Table S4 of the supplementary material.

### B. Photoinduced transformations of indole monomers isolated in Ne and Ar matrices

Monomers of indole, trapped in Ne and Ar matrices, were irradiated with UV (\(\lambda > 270\) nm) light (UG-11 cutoff filter, Fig. S1).\(^{51}\) This wavelength was chosen in accord with experimental UV spectra of indole in argon matrices,\(^{52-54}\) in solutions,\(^{55,56}\) and in the gas phase.\(^{57,58}\) Upon such irradiation, IR bands due to the initial 1H-tautomer decreased in intensity, while new bands, indicating generation of photoproducts, appeared in the spectrum. In order to identify the photoproducts, the experimental infrared spectrum consisting of the bands that emerged after UV irradiation was compared with the theoretical spectra of several candidate structures. The experimental spectrum of the photoproducts was very well reproduced by a superposition of the theoretical spectra of 3H-indole and the indolyl radical (Fig. 4). The theoretical spectrum of 3H-indole nicely fits the general pattern of the experimental IR bands, while the “additional” bands at 1557, 1179, and 759 cm\(^{-1}\) (Ne) or at 1555, 1177, and 758 cm\(^{-1}\) (Ar) correspond well to the strongest IR bands predicted for the indolyl radical. For any other candidate structures, the match between theoretical and experimental spectra is by far not so good.

These results clearly suggest that hydrogen-atom-transfer and hydrogen-atom-detachment processes strongly dominate the photochemical behavior of indole monomers trapped in solid noble-gas matrices. The two products (3H-indole and indolyl radical) photogenerated from 1H-indole, see Fig. 5.

![Diagram](image)

**FIG. 4.** Infrared spectra of photoproducts generated upon UV (\(\lambda > 270\) nm) irradiation of indole monomers isolated in (a) Ar and (b) Ne matrices, compared with (c) the theoretical spectra of 3H-tautomer of indole (black) and indolyl radical (red). The experimental spectra were obtained by subtraction of the spectra recorded before any irradiation (with intensities reduced by a scale factor) from the spectra recorded after UV (\(\lambda > 270\) nm) irradiation. In that way, the bands due to the unreacted part of the initial 1H-form were removed so that they do not obscure the spectrum of the photoproducts. The theoretical spectra were calculated within the harmonic approximation at the DFT(B3LYP)/6-311++G(d,p) level. The theoretical wavenumbers were scaled by 0.98. The experimental bands marked with red asterisks are spectral signatures of photogenerated indolyl radicals. Note two ordinate axes in frame (c).
are analogous of the two photoproducts (3H-tautomer and 7-azaindolyl radical) formed upon UV (λ > 270 nm) excitation of 7-azaindole. For the latter compound, the N7H-tautomer was also generated upon UV irradiation. The N1H → N7H phototautomerization in 7-azaindole is analogous to the UV-induced hydrogen-atom transfers from one heteroatom to the other, which were observed for a number of heterocyclic compounds. For indole, due to the lack of any heteroatom other than N1 in the structure, no species analogous to the N7H-tautomer, the formyl group is not co-planar with the indole ring lying in the symmetry plane. In the cis form, the C=O bond is nearly coplanar relative to the endocyclic C2=C3 bond (the O11=C10−C3=C2 dihedral angle equal to 120°), while in the trans form, these two bonds are aligned in an antiperiplanar fashion (the O11=C10−C3=C2 dihedral angle equal to 180°), see Figs. 1(b) and 1(c). In the structure of the 3H-tautomer, the formyl group is not coplanar with the indole ring. One of the identified conformers of 3H-Indole has a “minus” anticlinal orientation (ac−) of the formyl group (O11=C10−C3=C2 dihedral angle close to −120°), while the other conformer has a “plus” antyclinal orientation (ac+) of the formyl group (O11=C10−C3=C2 dihedral angle close to +120°), see Table S2 of the supplementary material.

At geometries optimized at the DFT(B3LYP)/6-311++G(d,p) level, the relative energies of the isomeric forms of 3FOI were calculated using the QCISD/6-311++G(d,p) method. The results of these calculations (given in Table S3 of the supplementary material) are graphically presented in Fig. 2. The lowest energy was computed for 1H-tautomer with a trans orientation of the formyl group, Fig. 1(b). The energy of the cis conformer of the same 1H-tautomer Fig. 1(c) was predicted to be higher by 5.1 kJ mol−1. The calculated corrections for zero-point-vibrational energy (as well as thermal and entropic corrections) are very similar in the 1H-trans and 1H-cis isomers. "C. Most stable isomers of 3-formylindole and their infrared spectra"

Similarly as in the case of unsubstituted indoles, nine prototropic tautomers are possible also for 3-formylindole (3FOI). Each of these 3FOI tautomers can adopt two conformational structures, differing in rotation of the formyl group around the C3−C10 bond. The geometries of all 18 isomers of 3FOI were optimized at the DFT(B3LYP)/6-311++G(d,p) level. The optimized structures are shown in Table S2 of the supplementary material. For all isomers of 3FOI, except two conformers of the 3H-tautomer, the optimized geometries have C₃₀ symmetry, with the formyl group and the indole ring lying in the symmetry plane. In the cis conformers, the C=O bond is nearly coplanar relative to the endocyclic C2=C3 bond (the O11=C10−C3=C2 dihedral angle equal to 0°), while in the trans conformers, these two bonds are aligned in an antiperiplanar fashion (the O11=C10−C3=C2 dihedral angle equal to 180°), see Figs. 1(b) and 1(c). In the structure of the 3H-tautomer, the formyl group is not coplanar with the indole ring. One of the identified conformers of 3H-Indole has a “minus” anticlinal orientation (ac−) of the formyl group (O11=C10−C3=C2 dihedral angle close to −120°), while the other conformer has a “plus” antyclinal orientation (ac+) of the formyl group (O11=C10−C3=C2 dihedral angle close to +120°), see Table S2 of the supplementary material.

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![FIG. 5. UV-induced hydrogen-atom detachment and hydrogen-atom transfer processes in indole. A and B represent the two dominant resonance hybrids of the indolyl radical with respect to the position of the unpaired electron. These structures and respective resonance weights (17% of A; 31% of B) were obtained from an NRT analysis at the UDF/B3LYP/6-311++G(d,p) level of theory. For details see Fig. S3 of the supplementary material.](image)

![FIG. 6. Optimized C−C and N−C distances in Å (red), natural bond orders (blue), and natural spin densities (green) calculated for the indolyl radical at the UDF/B3LYP/6-311++G(d,p) level. The natural bond orders and natural spin densities were obtained from a natural bond orbital (NBO) analysis.](image)
1H-cis isomers, and therefore they are expected to have very little influence on the relative stability.

The calculated energies of other prototropic tautomers, with the labile hydrogen atom moved from N1 to any of the carbon atoms of the indole ring, are substantially higher (by more than 50 kJ mol\(^{-1}\)), see Fig. 2 and Table S3 of the supplementary material) with respect to the energy of the most stable 1H-3FOI structure. This means that only 1H-trans and 1H-cis are expected to be non-negligibly populated in the gas phase at 350 K.

From the computed relative energies of 1H-trans and 1H-cis isomers of 3FOI, the relative Boltzmann populations of these two forms in the gas phase at 350 K can be estimated as ~85% of 1H-trans and ~15% of 1H-cis. The barrier for torsion of the formyl group in 1H-tautomer is quite high. As shown in Fig. S4 (in the supplementary material), it amounts to 35 kJ mol\(^{-1}\) (MP2) or 44 kJ mol\(^{-1}\) (DFT) for the 1H-cis → 1H-trans conversion and to 41 or 49 kJ mol\(^{-1}\) for the reverse transformation. Such values are typical of torsion of the formyl group connected to pyrrole or benzene rings. With a barrier as high as that and with the rotation of the formyl group involving significant displacement of heavy oxygen atoms, the gas-phase thermal equilibrium should be conserved after trapping the monomers of 3FOI in low-temperature matrices. Hence, the 1H-trans isomer of 3FOI is expected to be the most populated form of the compound isolated in Ar matrices, whereas the 1H-cis isomer should also be populated but in a considerably lower amount.

The infrared spectrum of monomers of 3FOI isolated in an Ar matrix is presented in Fig. 7(a), together with the spectra calculated for the 1H-trans and 1H-cis structures, Fig. 7(c). A list of the experimental and calculated wavenumbers and intensities as well as an approximate description of the vibration modes is given in Table S5 of the supplementary material. The experimental spectrum is very well reproduced by a sum [Fig. 7(b)] of the theoretical spectrum of 1H-trans (with IR intensities scaled by 0.85) and the theoretical spectrum of 1H-cis (with IR intensities scaled by 0.15). The experimental band at 948 cm\(^{-1}\) [marked with an asterisk in Fig. 7(a)] has no counterpart in the spectra computed within the harmonic approximation. In the anharmonic calculations performed for the 1H-trans isomer of 3FOI, a band due to the 2\(\gamma\)N1H overtone was predicted at 965 cm\(^{-1}\), with infrared intensity as high as 32 km mol\(^{-1}\). Hence, the experimental band at 948 cm\(^{-1}\) has been assigned to the 2\(\gamma\)N1H overtone. The band due to the fundamental \(\gamma\)N1H vibration was observed at 468 cm\(^{-1}\).

The theoretical spectra of 1H-trans and 1H-cis are quite similar to each other. Hence, just by a mere comparison with the theoretical prediction, it would be difficult to reliably assign particular experimental bands to the spectrum of one of the conformers. In this respect, the UV-induced conformational interconversion, described in Sec. IV D, was very useful. Thanks to this conformational transformation, it was possible to reliably assign a number of the non-overlapping experimental infrared bands to the spectra of the 1H-trans and 1H-cis forms.

D. Photoinduced transformations of 3-formyldiindole monomers isolated in Ar matrices

Monomers of 3FOI, trapped in Ar matrices, were exposed to UV (\(\lambda > 335\) nm) radiation (WG-335 cutoff filter, Fig. S1 of the supplementary material).\(^{51}\) This wavelength was chosen in accord with the UV spectra of 3FOI in solutions.\(^{67,68}\) The main effect of such irradiation was the decrease of the strongest bands in the infrared spectrum of the compound, accompanied by intensity increase of a set of weaker bands. The observed spectral changes are illustrated in Figs. 8(a) and 8(b). Comparison with the theoretically simulated spectra of 1H-trans and 1H-cis isomers of 3FOI [Fig. 8(c)] leaves no doubt that the main photochemical process occurring upon UV (\(\lambda > 335\) nm) irradiation of matrix-isolated 3FOI is the conformational conversion transforming the 1H-trans isomer into the 1H-cis form (see Fig. 9). Subsequent irradiation at slightly different UV wavelengths (\(\lambda > 320\) nm) demonstrated that this conformational isomerization is partially photoreversible.
An attempt has been undertaken to induce the 1H-trans ↔ 1H-cis interconversion by excitation of matrix-isolated 3FOI with near-IR light. The idea was similar to that employed for rotation of the methoxy group of 6-methoxyindole or 5-methoxyindole by near-IR excitations of the 2νN1H overtone.\textsuperscript{69,70} For this purpose, the near-IR spectrum of 3FOI isolated in an Ar matrix was recorded (Fig. S5 of the supplementary material). The band due to the 2νN1H overtone was detected in this spectrum as a near-IR absorption split into three components (6876, 6870, and 6864 cm\(^{-1}\)). The shape of this overtone band reflects the shape (split into three components 3506, 3503, and 3501 cm\(^{-1}\)) of the band due to the fundamental vN1H vibration [Figs. S5(a) and S5(b)].

Irradiation of monomers of 3FOI isolated in an Ar matrix with monochromatic near-IR light at 6876, 6870, and 6864 cm\(^{-1}\) did not result in any change of populations of 1H-trans and 1H-cis conformers of 3FOI (Fig. S6 of the supplementary material). The energy introduced to the molecule by absorption of the near-IR photon (with wavenumber 6890-6860 cm\(^{-1}\)) is higher than 80 kJ mol\(^{-1}\). This is approximately twice as much as the height of the barrier calculated for the cis ↔ trans isomerization in both directions (Fig. S4 of the supplementary material). Although such energy should, in principle, be more than sufficient to induce a conformational isomerization in 1H-3FOI, an efficient mechanism of vibrational energy transfer, from the initially excited N1H stretching mode to the remote C3—C10 torsional mode, is also necessary. The experimental results obtained for matrix-isolated 3FOI clearly show that the vibrational energy transfer from the excited N1H stretching overtone to the torsion around the C3—C10 bond is not efficient enough to promote the 1H-cis ↔ 1H-trans isomerization by the internal rotation of the formyl group.

UV (\(\lambda > 335\) nm) irradiation of matrix-isolated 3FOI resulted not only in the transformation of 1H-trans conformer into 1H-cis form. Besides the spectral changes resulting from this dominating phototransformation, several new bands emerged in the infrared spectrum recorded after UV (\(\lambda > 335\) nm) irradiation [Fig. 10(a)]. These bands indicate that a photoproduct other than the 1H-trans or 1H-cis isomer was photogenerated. The most intense of the new bands were found at 1733 and 763 cm\(^{-1}\). The wavenumber 1733 cm\(^{-1}\) is typical of stretching vibrations of carbonyl C=O groups (vCO), but this frequency is significantly higher than the spectral position of the vCO band(s) in the spectra of 1H-trans and 1H-cis isomers of 3FOI. In the infrared spectra calculated for the cis and trans conformers of 2H, 4H, . . . , 9H tautomers of 3FOI, the vCO band is predicted at frequencies ranging from 1678 to 1706 cm\(^{-1}\) (see Table S6 of the supplementary material). Such frequencies are similar to or below the frequency computed for 1H-trans and 1H-cis isomers (1702 cm\(^{-1}\)). Exceptionally high frequency of the vCO vibration was predicted only for two 3H-ac\(^{-}\) and 3H-ac\(^{+}\) conformers of 3H-tautomer (see Fig. 10(b) and Table S6 of the supplementary material). Note that in the structures of 3H-ac\(^{-}\) and 3H-ac\(^{+}\), the formyl group is not co-planar with the indole ring, as it is the case for other isomers of 3FOI (Fig. 9 and Table S2 of the supplementary material). This significant geometry difference causes different electronic coupling between the formyl group and the indole ring. As a consequence, the frequencies of the vCO vibrations in 3H-ac\(^{-}\) and 3H-ac\(^{+}\) are significantly different (higher) in comparison to the frequencies of analogous vCO vibrations in other (\(C_\alpha\)) isomers of 3FOI.

![FIG. 8. (a) Selected regions of the experimental mid-IR spectrum of 3FOI monomers isolated in an Ar matrix at 15 K: (red trace) recorded before any UV irradiation and (blue trace) recorded after 150 minutes of UV (\(\lambda > 335\) nm) irradiation; (b) the spectrum recorded after UV (\(\lambda > 335\) nm) irradiation minus the spectrum recorded before any irradiation; (c) simulated spectra of two conformers of 1H-3FOI: 1H-cis (orange trace) and 1H-trans (with the intensities multiplied by ~1, violet trace). The theoretical spectra were calculated within the harmonic approximation at the DFT(B3LYP)/6-311++G(d,p) level. The theoretical wavenumbers higher than 3200 cm\(^{-1}\) were scaled by 0.95, and the wavenumbers lower than 3200 cm\(^{-1}\) were scaled by 0.98.](image_url)

![FIG. 9. Phototransformations of 1H-3FOI monomers isolated in low-temperature Ar matrices and excited with UV (\(\lambda > 335\) nm) light.](image_url)
revealed three types of photochemical behavior: isolated in low-temperature noble-gas matrices. These studies been investigated for monomers of indole and 3-formylindole.

V. CONCLUSIONS

process occurring in indole and substituted indoles isolated in low-temperature matrices.

(ii) Hydrogen-atom detachment from the N1—H bond, leading to the generation of indolyl radicals. The indolyl radical was directly observed as a product emerging upon UV excitation of matrix-isolated indole. In the case of 3-formylindole, no clear IR spectral indication of generation of analogous radicals was found, but the low-intensity bands of this product may be obscured by the densely spaced spectrum of two conformers of this compound. Radicals resulting from hydrogen-atom detachment from the N1—H bond were observed for several compounds with the structure similar to indole: 7-azaindole, carbazole, and 6-methoxyindole. All these observations corroborate the conclusions that indolyl radicals (and analogous radicals) are photogenerated from indole (or substituted indoles) and that these radicals are stabilized in low-temperature inert-gas matrices. Observation of indolyl radicals produced upon UV excitation of matrix-isolated indole is consistent with the results of photochemical behavior of indole in the gas phase (supersonic jets). The photofragment translational spectroscopy experiments demonstrated that detachment of slow and fast hydrogen atoms from the N—H group is the basic photochemical process occurring in UV-excited indole molecules in the gas phase.

The tendency of indole, 3-formylindole, and other indole derivatives to undergo hydrogen-atom transfer from N1 to C3 seems to be strongly related with the formation of C3-centered radicals, which facilitate the reattachment of the labile hydrogen atom at this position. The strongly marked reactivity of the indolyl radicals at the C3 position was elucidated by the natural resonance theory analyses.

(iii) Conformational $1H$-trans $\leftrightarrow 1H$-cis phototransformation by rotation of the aldehyde group in 3-formylindole. This conformational change, occurring upon UV excitation of 3-formylindole, was photoreversible and led to a photostationary population ratio of $1H$-trans and $1H$-cis isomers. UV-induced rotation of the aldehyde group in 3-formylindole is similar to the photoisomerizations observed for pyrrole-2-carbaldehyde and salicylaldehyde isolated in low-temperature matrices.

In the progress of the photochemical studies carried out within the current work, the infrared spectra of matrix-isolated indole, indolyl radical, and two conformers of 3-formylindole were characterized. To the best of our knowledge, the experimental infrared spectra of these matrix-isolated compounds are reported here for the first time. The same is true for the spectra of the photogenerated $3H$-prototropic tautomers: $3H$-indole and $3H$-3-formylindole.

SUPPLEMENTARY MATERIAL

See supplementary material for the structures of indole and 3FOI isomers, their theoretically assessed relative...
energies and barriers for the rotation of the formyl group; resonance structures, natural spin densities, and natural bond orders of indolyl and 3-formylindolyl radicals; fragments of mid-IR and near-IR spectra of 3FOI; internal coordinates used in the PED analysis; characteristics of the cutoff filters used for UV irradiations.

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present conformational analysis, it has been arbitrarily assumed that the 3H-3FOI tautomer is formed as the S-enantiomer. The 3H-ac⁺ and 3H-ac⁻ conformational names apply then to the S absolute configuration.
